

PATENT SPECIFICATION



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COMPLETE SPECIFICATION.

The Manufacture of New Azo Dyestuffs.

We, I. G. FARBENINDUSTRIE AKTIEN-GESELLSCHAFT (formerly known as Badische Anilin & Soda Fabrik), a company organised under the laws of Germany, of Frankfurt-on-Main, Germany (Assignees of FARBENFABRIKEN vorm. Friedr. Bayer & Co., a company organised under the laws of Germany, of Leverkusen, near Cologne-on-Rhine, Germany), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the manufacture of new triazo. dyestuffs.

According to this invention an amino-azo compound produced from an acidyl-*p*-diamine or *p*-nitramine and a further diazotizable middle component is combined with a derivative of an aminonaphthol sulphonic acid, such for example as 2,5-, 2,8- or 1,8-aminonaphthol sulphonic acids containing a free heteronuclear amino group, then further diazotised and coupled with methylketol or with 3-methyl-1-phenyl-5-pyrazolone or derivatives thereof and subsequently either splitting off the acidyl group or as the case may be reducing the nitro group of the starting component. The dyestuffs thus produced give direct dyeings in green shades, instead of the violet to blue shades hitherto obtained with the dyestuffs made according to the process described in Specification No. 974/1911.

The following examples serve to illustrate the invention which is of course applicable within very wide limits.

EXAMPLE 1.

23 parts by weight of 4-acetylamino-1-aminobenzene-2-sulphonic acid are dissolved with the addition of sodium carbonate to give a neutral solution and diazotised at 10° C. with 30 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite. The diazo solution is caused to run into a neutral solution of 26.7 parts by weight of 1,2-aminonaphthoethylether-6-sulphonic acid to which sodium acetate has been added. The isolated inter-

mediate product is again made into a paste and is converted into the sodium salt with 25 parts by weight of 16% caustic soda lye and is then diazotised at about 15° C. with 69 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite. The isolated diazotization product is coupled whilst in a concentrated condition at 0° C. with 30.5 parts by weight of *p*-aminobenzoyl-2-amino-5-naphthol-7-sulphonic acid. The disazo dyestuff is carefully isolated, made again into a paste and subjected to further diazotisation with 69 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite and coupled with 13.0 parts by weight of 3-methyl-1-phenyl-5-pyrazolone rendering alkaline with sodium carbonate. On heating in weak alkaline or acid solution the acetyl group is split off and the finished dyestuff is isolated in the customary manner. It dyes direct in a very clear green shade which is slightly changed after development with β -naphthol or 3-methyl-1-phenyl-5-pyrazolone.

EXAMPLE 2.

The coupled and further diazotised monoazo dyestuff obtained as described in Example 1 from 23 parts by weight of 4-acetylaminoaniline-2-sulphonic acid and 26.7 parts by weight of 1,2-aminonaphthol-ethylether-6-sulphonic acid is coupled whilst in a concentrated condition at 0° C. with 30.5 parts by weight of *p*-amino-benzoyl-2-amino-8-naphthol-6-sulphonic acid, maintaining a weakly alkaline reaction by means of ammonia. The dyestuff is isolated with common salt and is further diazotised with 69 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite at about 15° C. and is combined in acid solution with 10.0 parts by weight of methylketol. The acetyl group is split off by heating in weak acid or alkaline solution and the dyestuff is then isolated in the customary manner after rendering alkaline with sodium carbonate. It gives direct dyeings of a green shade which remain nearly unchanged after develop-

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ment with β -naphthol or 3-methyl-1-phenyl-5-pyrazolone.

EXAMPLE 3.

28 parts by weight of 1.4-acetylnaphthylene-diamine-6-sulphonic acid are dissolved with sodium carbonate to give a neutral solution and diazotised at about 15° C. with 30 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite. The diazo product is coupled in acetic acid solution with a solution of 22.3 parts by weight of 1.6-naphthylamine sulphonic acid. This intermediate azo compound is further diazotised at room temperature with 69 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite and is coupled after the addition of sodium carbonate with a solution of 35.8 parts by weight of *p*-aminobenzoyl - 1 - amino - 8 - naphthol - 4 - sulphonic acid. The dyestuff after salting out is again made into a paste and further diazotised at 18° C. with 69 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite and coupled after the addition of sodium carbonate with 17.4 parts by weight of 3-methyl-1-phenyl-5-pyrazolone. The isolated dyestuff is heated in weak acid or alkaline solution whereby the acetyl group is split off and the final product is isolated in the customary manner. It gives direct dyeings of a green shade which remains unchanged after development with β -naphthol or 3-methyl-1-phenyl-5-pyrazolone.

The *p*-aminobenzoyl - 1 - amino - 8 - naphthol-4-sulphonic acid referred to above is prepared in the known manner by the reaction of *p*-nitrobenzoylchloride upon 1 - amido - 8 - naphthol - 4 - sulphonic acid (sodium salt) in a weakly alkaline solution with following reduction of the reaction product thus obtained with the aid of iron in acetic acid solution.

EXAMPLE 4.

26 parts by weight of 4-oxalylamino-1-aniline-3-sulphonic acid are dissolved with the addition of sodium carbonate to form a neutral solution and diazotised at 10° C. with 30 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite, coupled with an acid solution of 18.7 parts by weight of 1.2-aminonaphthol-ether and acetate solution is added until the acid reaction indicated by congo red has ceased. The aminoazo compound after being isolated in a state showing reaction to congo red is further diazotised with 69 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite and the isolated diazo compound coupled in a concentrated condition at 0° C. in

solution weakly alkaline with ammonia with 30 parts by weight of *m* or *p* aminophenyl - 1 : 2 - naphthimidazole - 5 - oxy - 7-sulphonic acid. The isolated dyestuff is further diazotised at ordinary temperature with 69 parts by weight of commercial hydrochloric acid and 6.9 parts by weight of sodium nitrite and coupled with 10 parts by weight of methylketol. The oxalyl group is split off in a manner analogous to that described in the foregoing examples and the dyestuff is isolated in the customary manner after rendering alkaline with sodium carbonate. It gives direct dyeings of a blueish green shade, which after development with β -naphthol changes into a greyish green shade and after development with 3-methyl-1-phenyl-5-pyrazolone into a green shade.

Instead of the acetyl *p*-phenylene-diamine sulphonic acid, described in Example 1 other acetylated *p*-phenylene or naphthalene diamines or also their halogen, oxalkyl, sulpho or carboxylic acid derivatives may be used.

As middle components the following may be mentioned as being particularly suitable: Aminocresol ether, α -naphthylamine, α -naphthylamine - 6 - or 7 - sulphonic acids, 1.5-aminonaphthol-7-sulphonic acid, 1.2-aminonaphtholether and its sulphonic acids, it being understood that the diazotisation components of the naphthalene series are more advantageously coupled with α -naphthylamine and its derivatives and that those of the benzene series are coupled likewise more advantageously with the aminocresol- or naphtholethers.

Instead of the aminobenzoyl-2-amino-5-naphthol-7-sulphonic acid other derivatives of 2.5-, 2.8- or 1.8-aminonaphthol-mono- or disulphonic acids containing free heteronuclear amino groups may be employed, as for example, aminobenzoyl-, aminophenyl - naphthimide - azole - and aminophenyl-naphthothiazole derivatives of the aminonaphthol sulphonic acids before-mentioned.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The manufacture of new trisazo dyestuffs by coupling an aminoazo compound obtained from a *p*-nitramine or acidyl *p*-diamine or a derivative thereof and a further diazotisable middle component with a derivative of an aminonaphthol sulphonic acid containing a free heteronuclear amino group, further diazotising the resulting disazo dyestuffs and coupling with methylketol or 3-methyl-1-

phenyl-5-pyrazolone or a derivative thereof and either splitting off the acidyl group, or as the case may be, reducing the nitro group of the starting component.

5 2. The manufacture of new azo dyestuffs substantially as described with reference to the foregoing examples.

3. The new azo dyestuffs whenever pre-

pared or produced in the manner claimed in Claim 1 or 2 or by their obvious chemical equivalents.

Dated the 16th day of September, 1926.

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